Detection of G-Series and VX Chemical Warfare Agent Degradation Products in Water by Solid Phase Microextraction

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Abstract

- The ability to detect the presence of Chemical Warfare agents in a variety of matrices is important for the protection of both military and civilian populations.

- We looked at the hydrolysis products of the GB, GD, and VX agents using Solid Phase Microextraction (SPME).

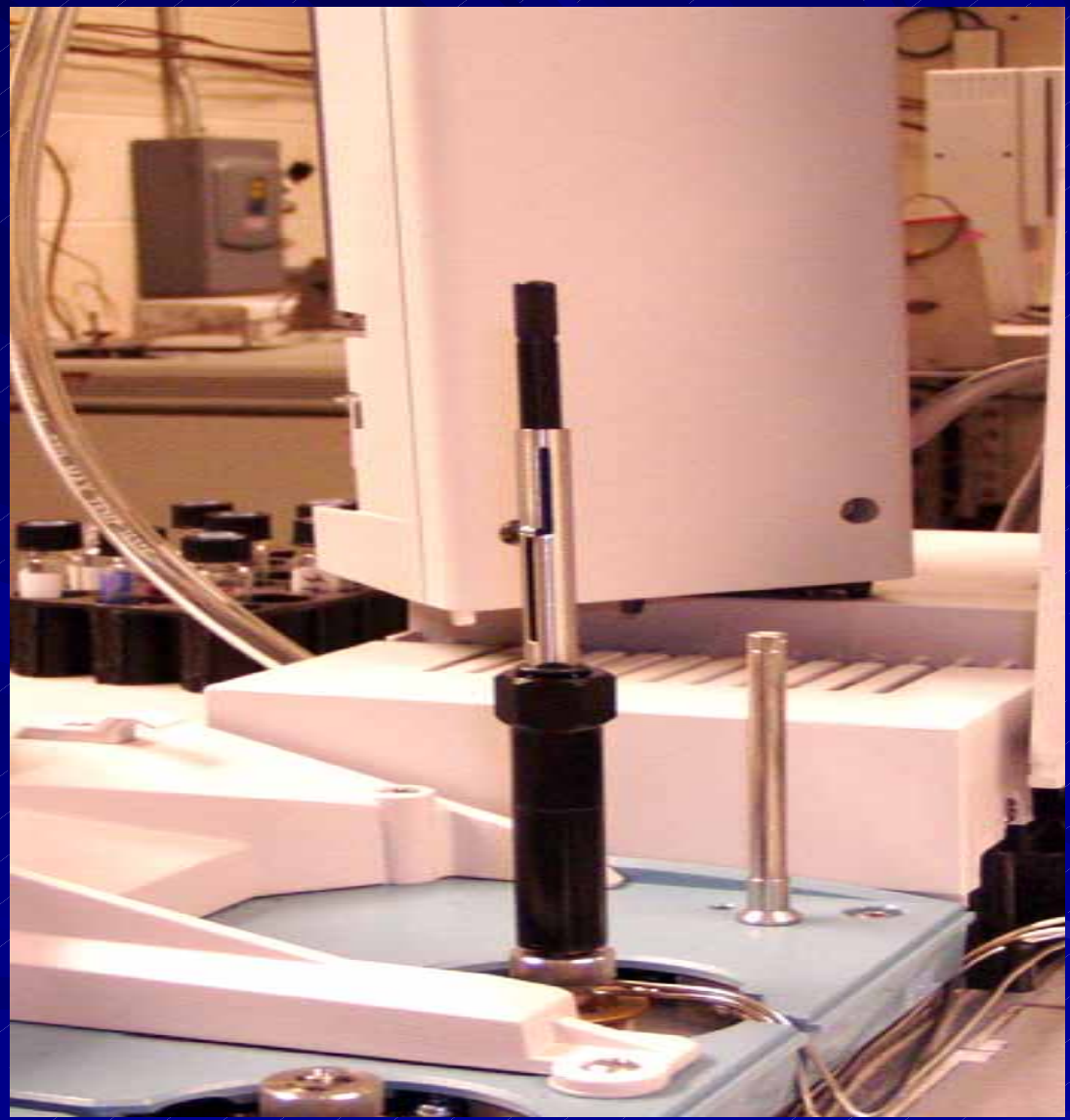
Hydrolysis Products

- Isopropyl Methyphosphonate (IMP)
  - GB (Sarin)
  - Isopropyl methylphosphonofluoridate
- Pinacolyl Methylphosphonate (PMP)
  - GD (Soman)
  - Pinacolyl Methylphosphofluoridic Acid
- Ethyl Methylphosphonate (EMP)
  - VX
  - O-ethyl-S-[2-diisopropylaminoethyl] methylphosphonic acid

Instrumentation

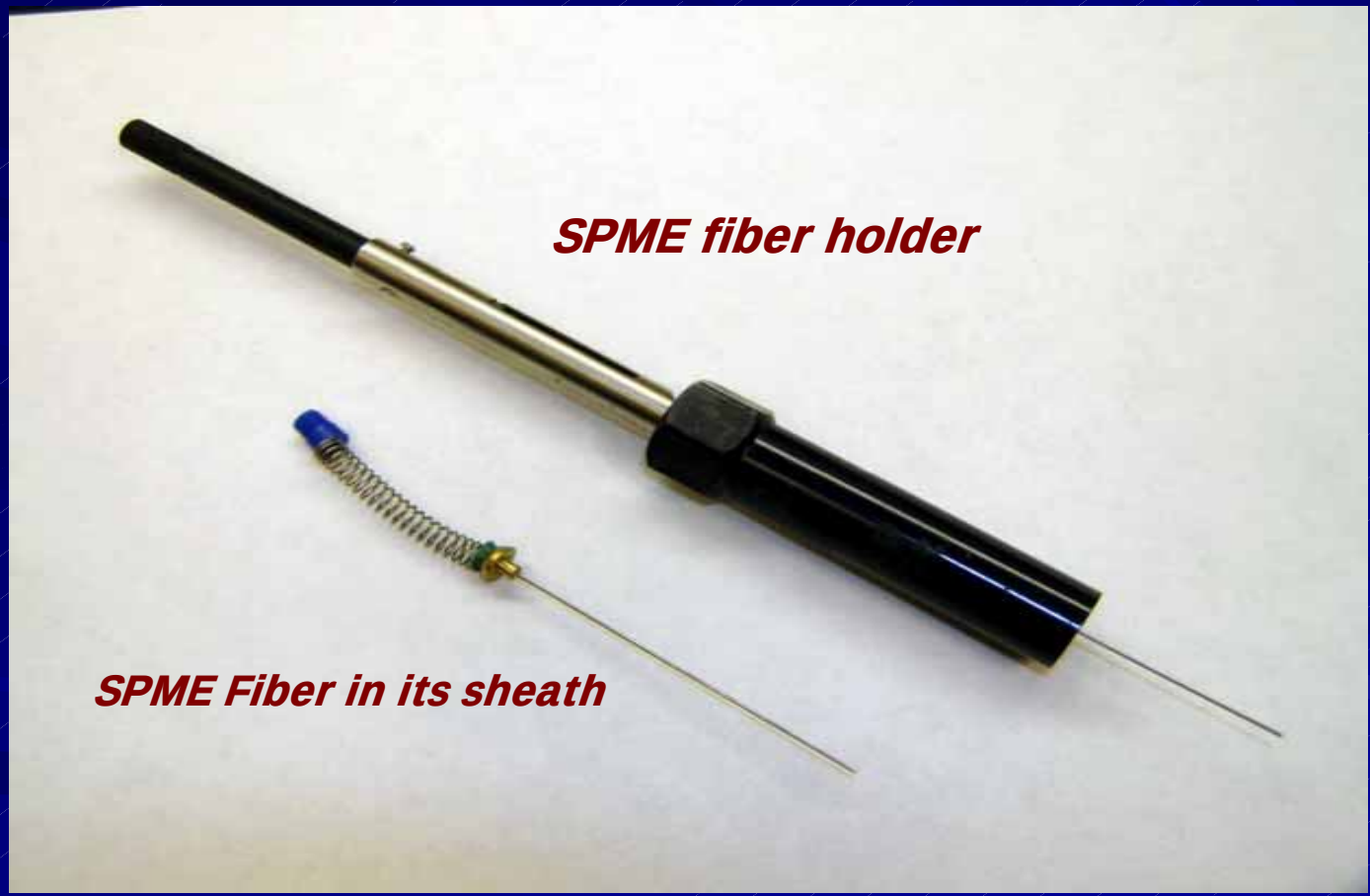
- Gas Chromatograph
  - Agilent 5890 Gas Chromatograph
  - Merlin Microseal Septum
  - Unis 2000 Injection Port
- Mass Spectrometer
  - Agilent 5973 Mass Selective Detector (MSD)
  - Inert Source

SPME

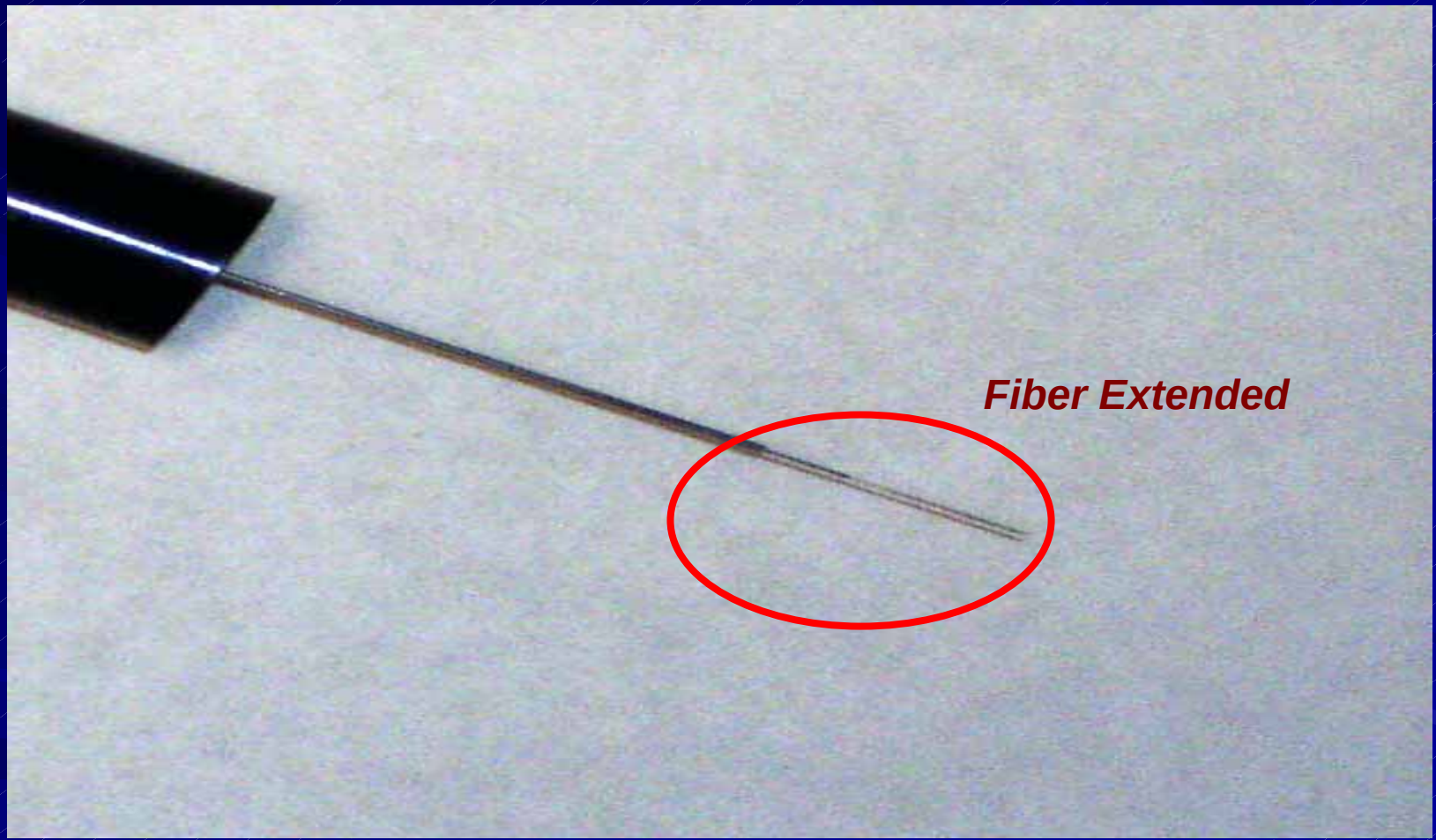


Injection Port Liners

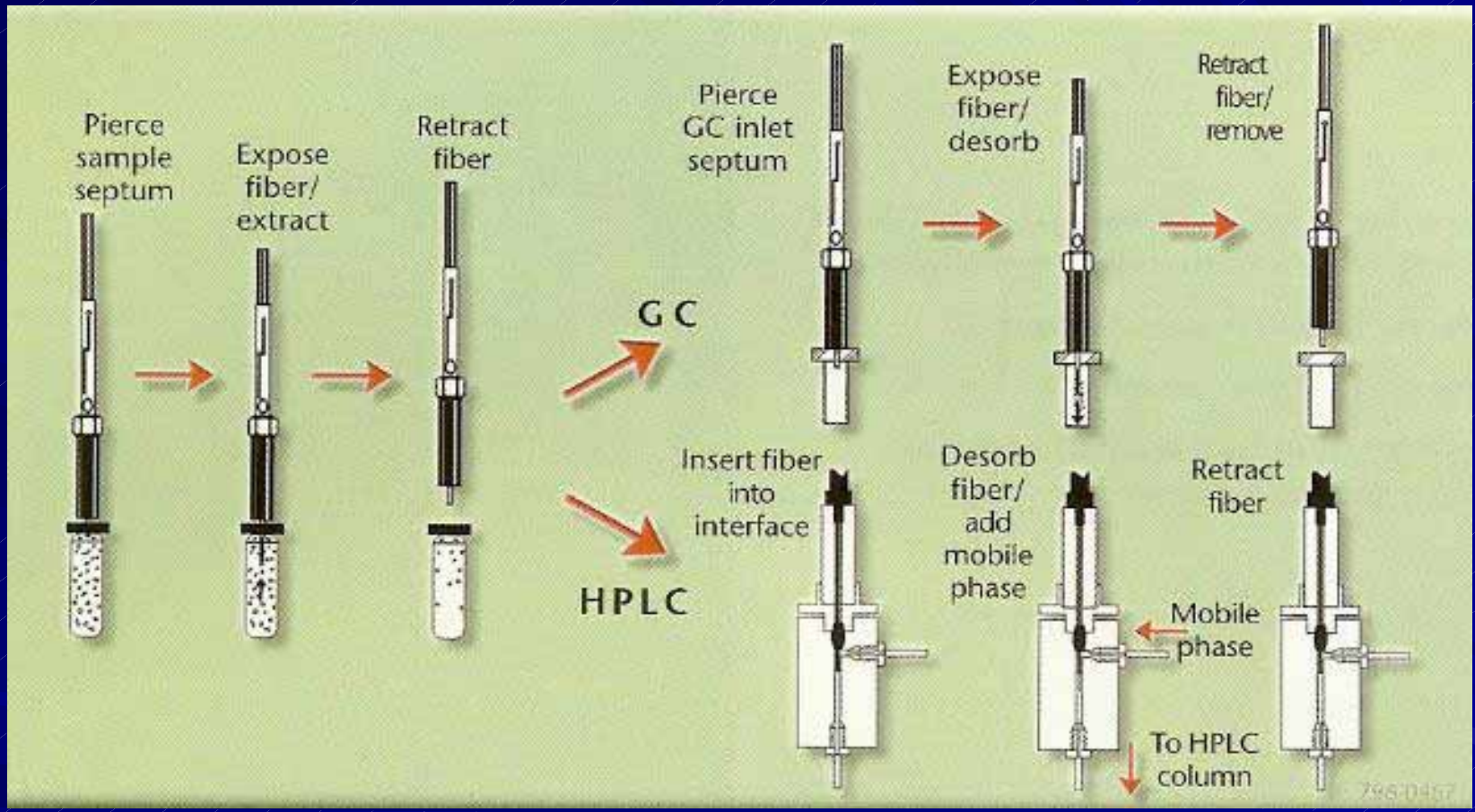
SPME Fiber and the Holder
(Solid Phase Micro-Extraction)



SPME Fiber Extended



SPME Process



SPME

SPME Fiber Extended into the Solution on Stir Plate Showing the Fiber Placement in the Vortex

GC Conditions

- GC/MS conditions.
  - Chromatographic conditions.
    - 15 M x 0.25 mm DB-1701 column with a 0.25 µm Film.
    - Injector temperature: 180^{o} C
    - 2 minute valve time
    - Oven was held at 40^{o} C for two minutes.
    - Oven then ramped: 40^{o} C to 180^{o} C at 16^{o} C/minute
    - Carrier: Helium with a flow of 2 mLs/minute

Mass Spec Conditions

- Agilent 5973 MSD
- New Agilent Inert Source
  - Improved Sensitivity
  - Improved Peak Shape
- Solvent delay: 2 minutes
- Mass Spectra were collected in SIM mode.

Selected Ions

- Ethyl Methylphosphonate
  - Target Ion 97 Dwell Time 100 μseconds
  - Qualifier Ion 125 Dwell Time 100 μseconds
- Isopropyl Methylphosphonate
  - Target Ion 97 Dwell Time 100 μseconds
  - Qualifier Ion 79 Dwell Time 100 μseconds
  - Qualifier Ion 125 Dwell Time 100 μseconds
- Pinacolyl Methylphosphonate
  - Target Ion 123 Dwell Time 100 μseconds
  - Qualifier Ion 124 Dwell Time 100 μseconds

SPME Fibers

- Tested various fibers:
  - Carbowax (CW)
  - Carboxen/Polydimethylsiloxane (CAR/PDMS)
  - Polydimethylsiloxane/Divinylbenzene (PDMS/DVB)
  - Polyacrylate
  - Polydimethylsiloxane (PDMS)

SPME Test Conditions

- The fibers were tested under four conditions.
  - Water
  - Water with 1 gram of Sodium Chloride
  - Water at pH 4.0
  - Water at pH 4.0 with 1 gram of Sodium Chloride
- The best results were obtained with the addition of Sodium Chloride.

Fibers (with 1 gram of NaCl) vs Mass Spec. Response

Fiber	IMP	EMP	PMP
Carbowax	1056163	770625	1784830
Carboxen/PDMS	5745663	2392218	5335299
PDMS/DVB	16348626	3893553	7222908
Polyacrylate	859319	No Peak	3702256
Polydimethylsiloxane	2644239	859467	5427659

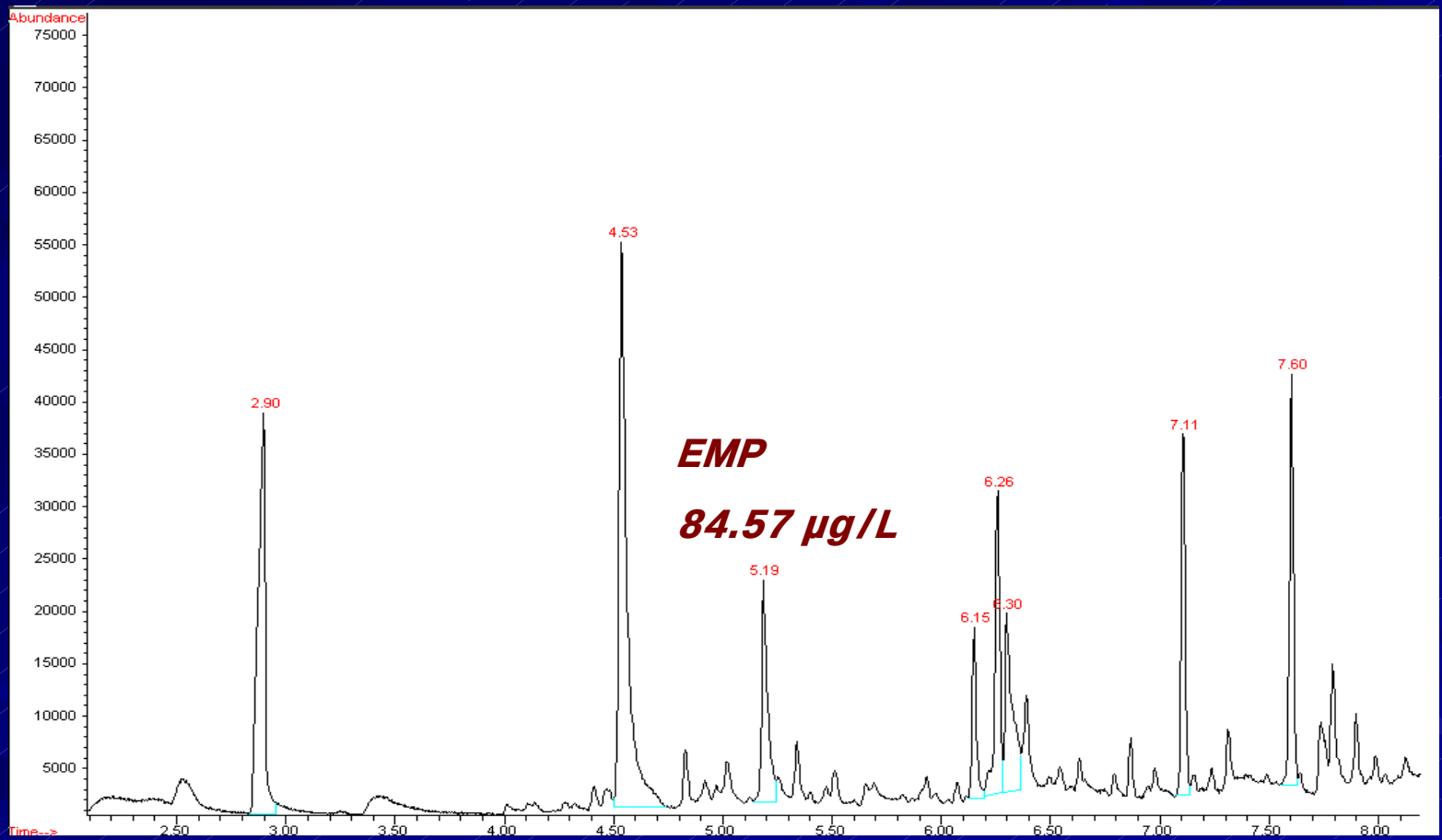
SPME Conditions

- Sample Size: 3 milliliters
- 1 gram sodium chloride added to the sample.
- Extraction time: 30 minutes
- Desorbtion temperature: 180^{o}C
- Desorbtion time: 2 minutes

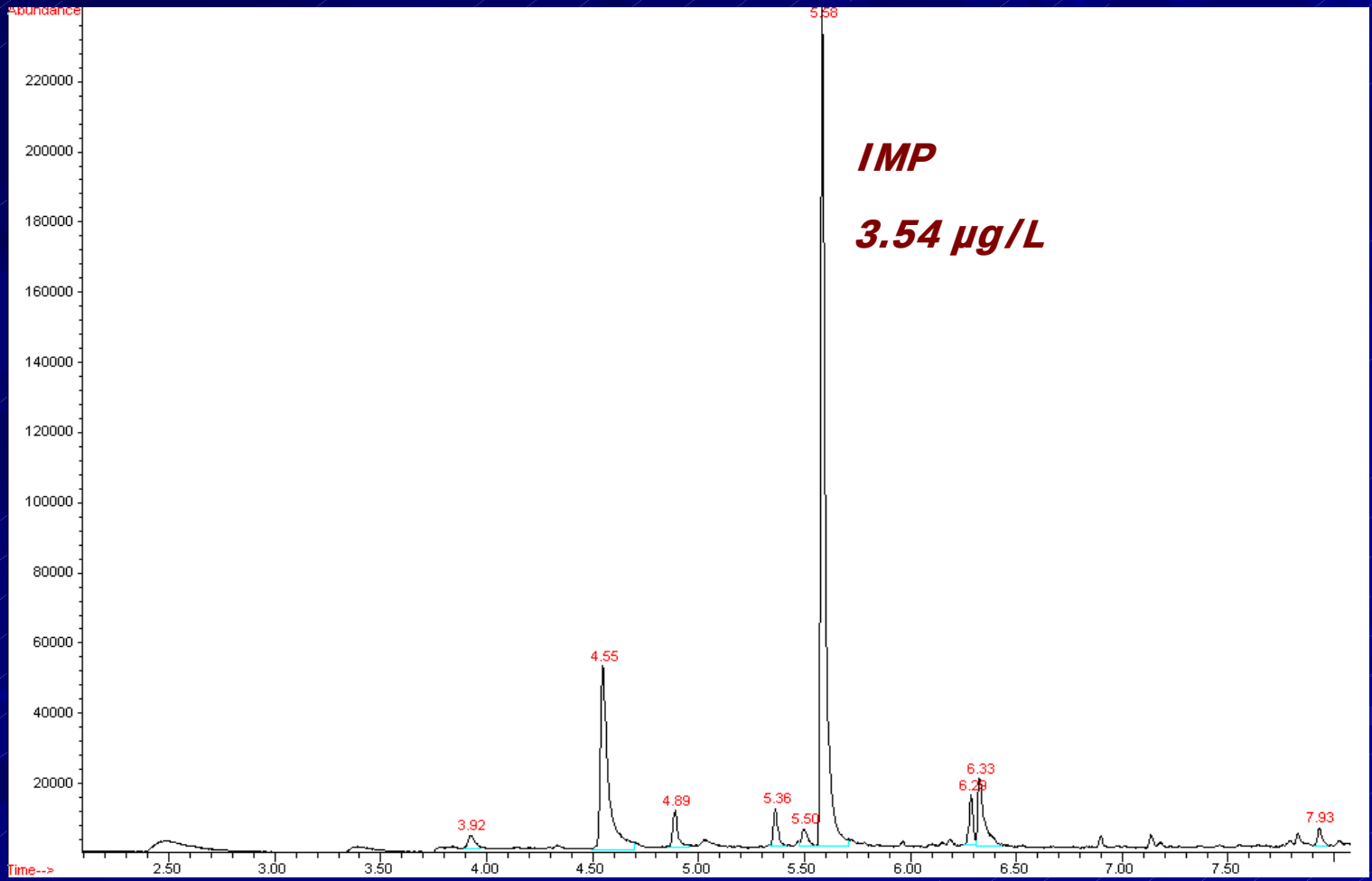
Retention Times

Compound	*Retention Time*
Ethyl Methylphosphonate	**5.19 minutes**
Isopropyl Methylphosphonate	**5.58 minutes**
Pinacolyl Methylphosphonate	**8.39 minutes**

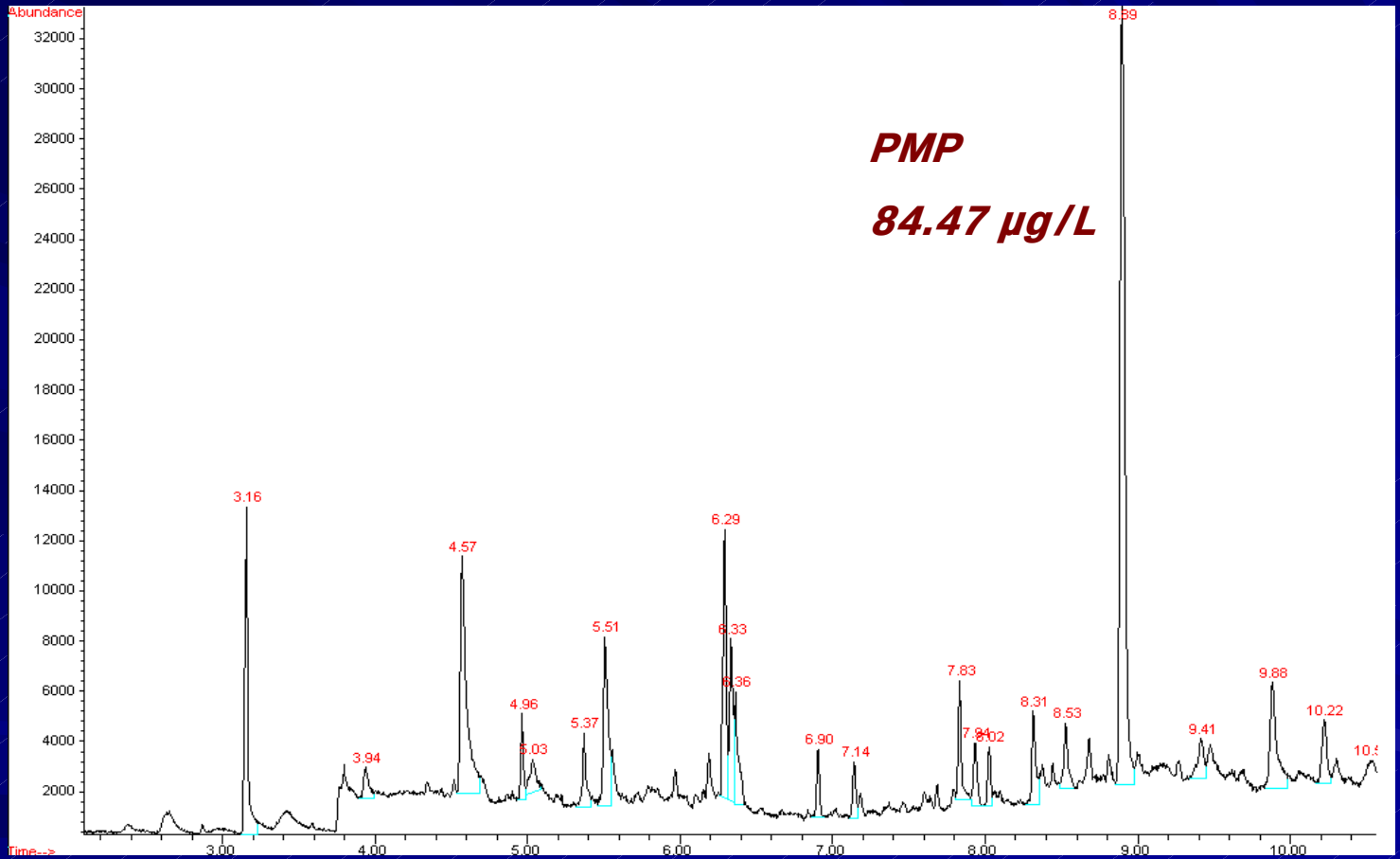
EMP Chromatogram



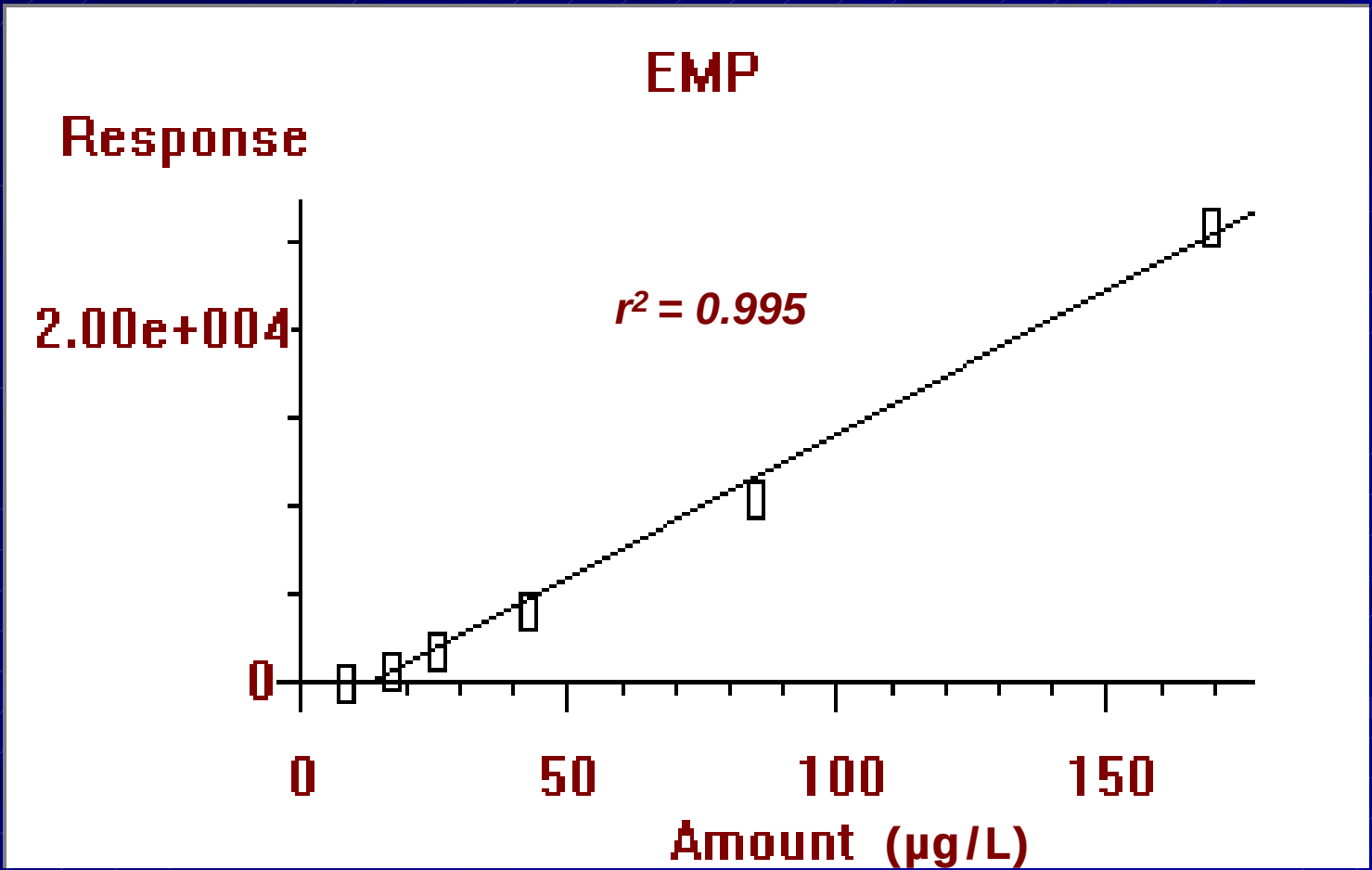
IMP Chromatogram



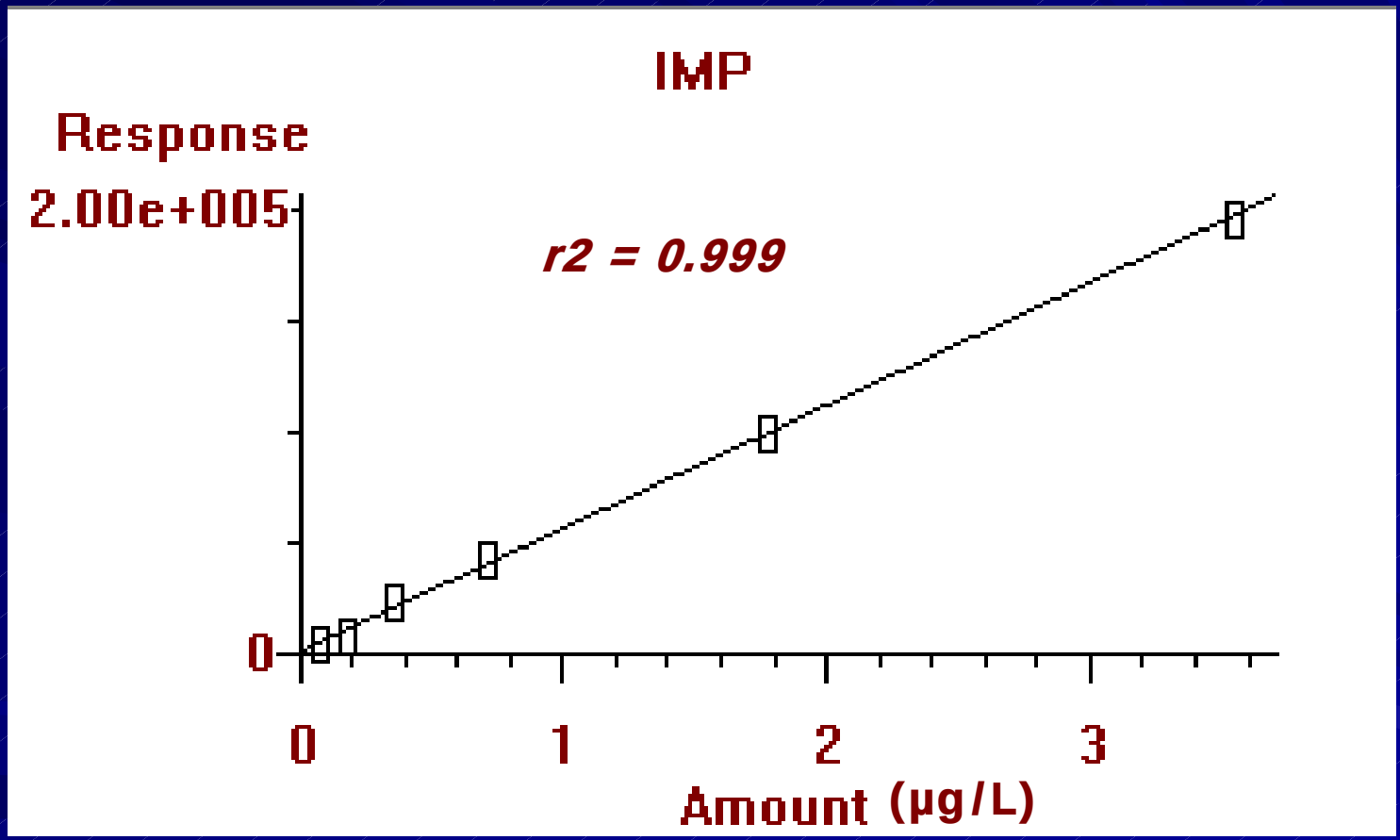
PMP Chromatogram



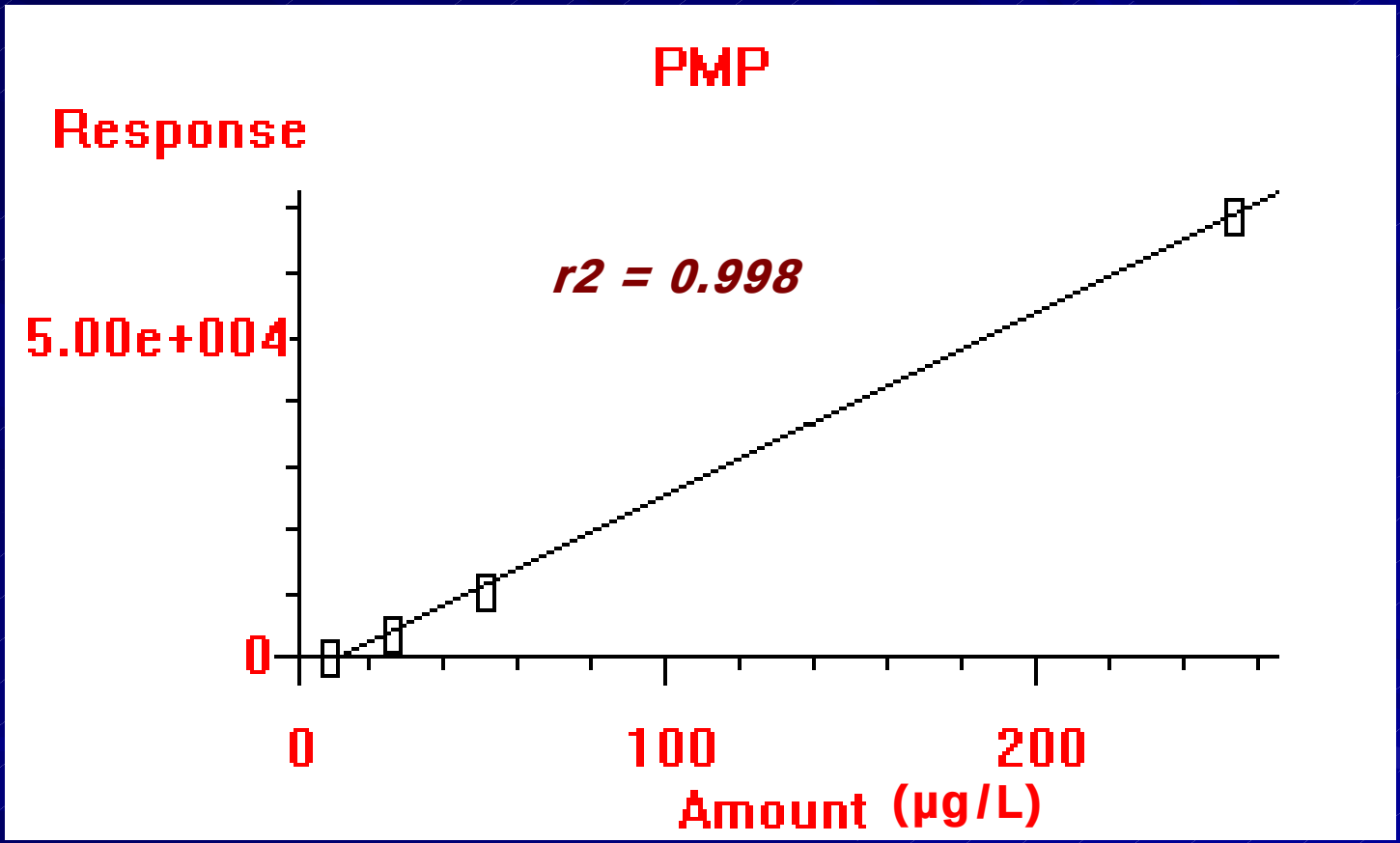
EMP Standard Curve



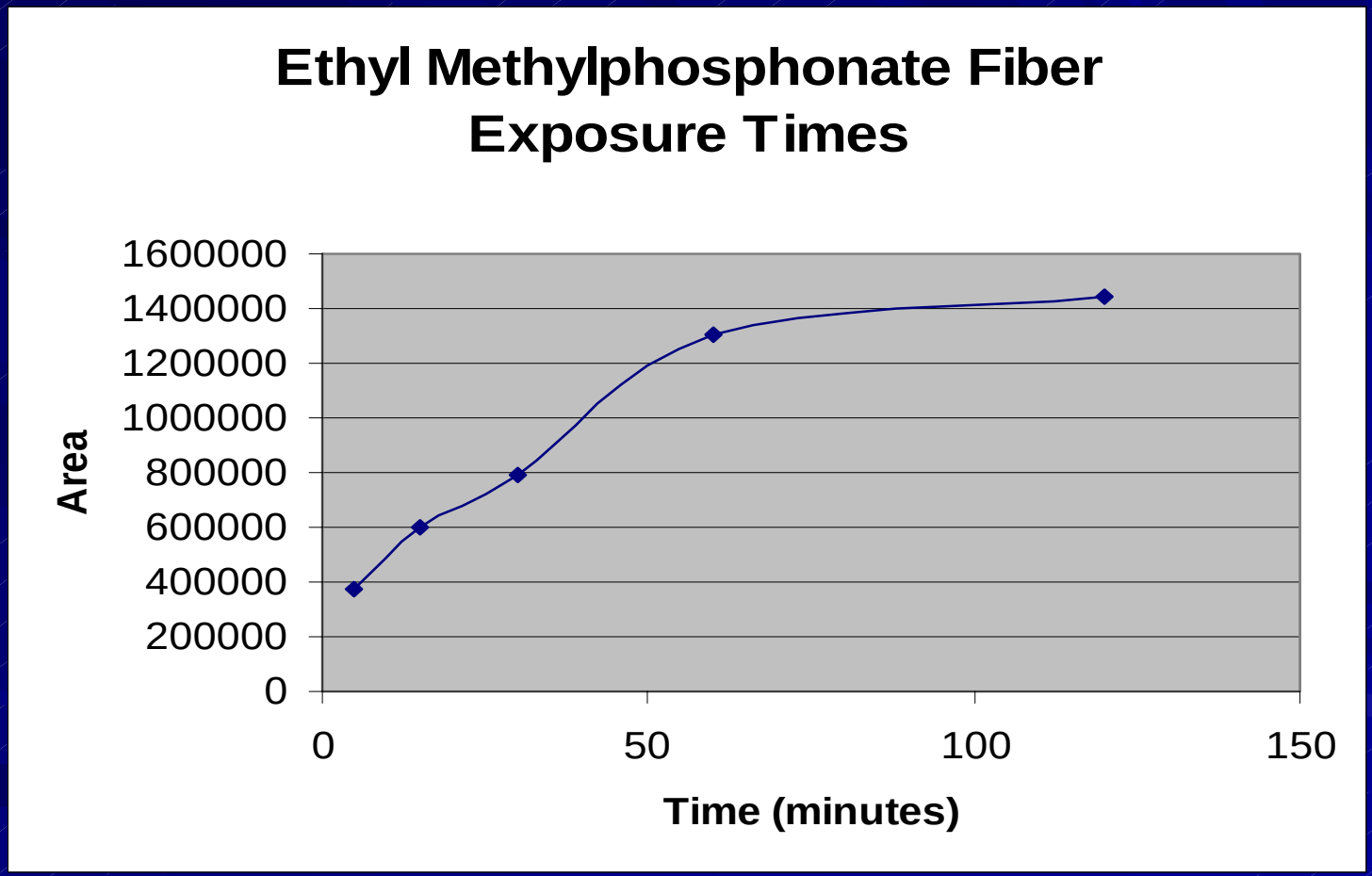
IMP Standard Plot



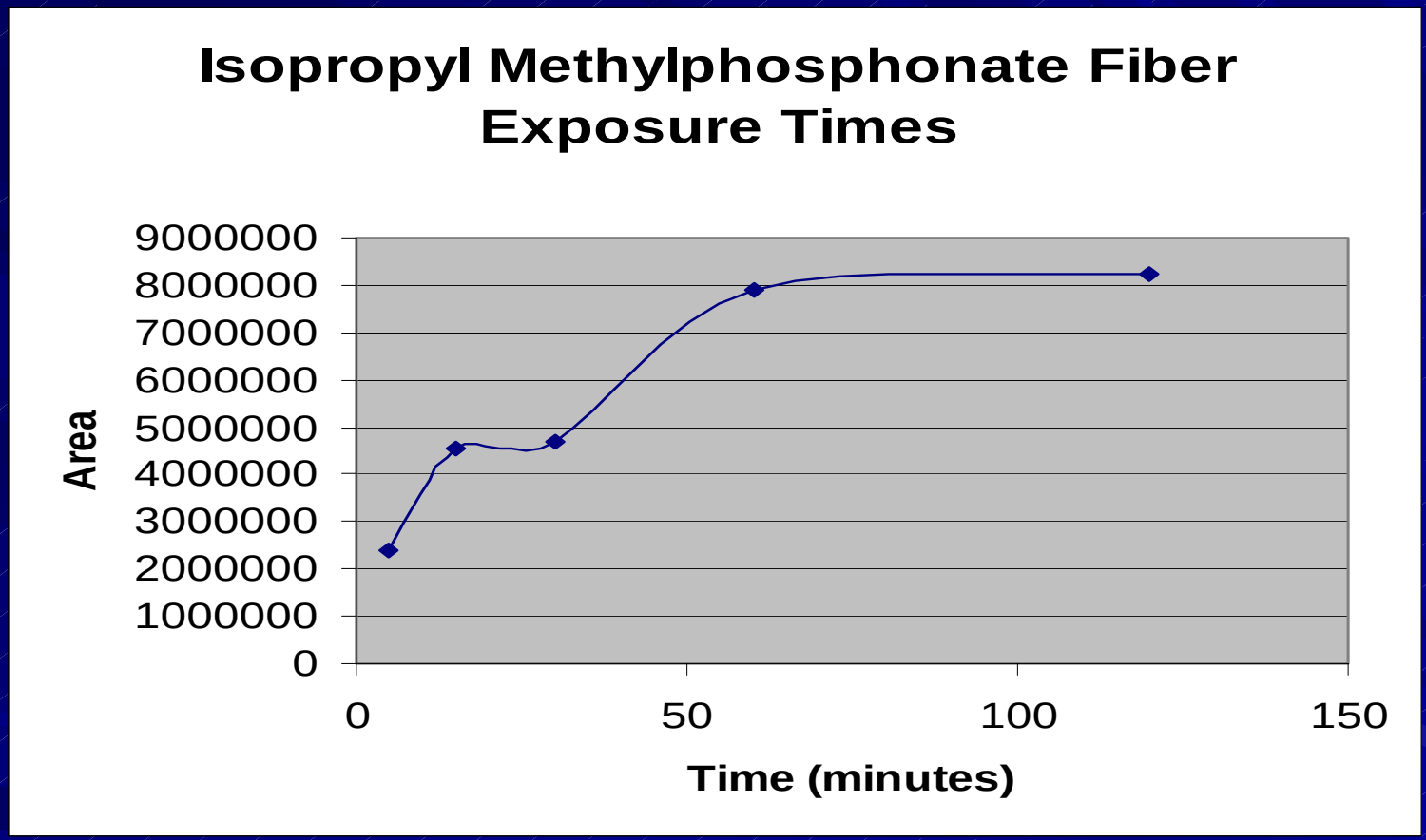
PMP Standard Plot



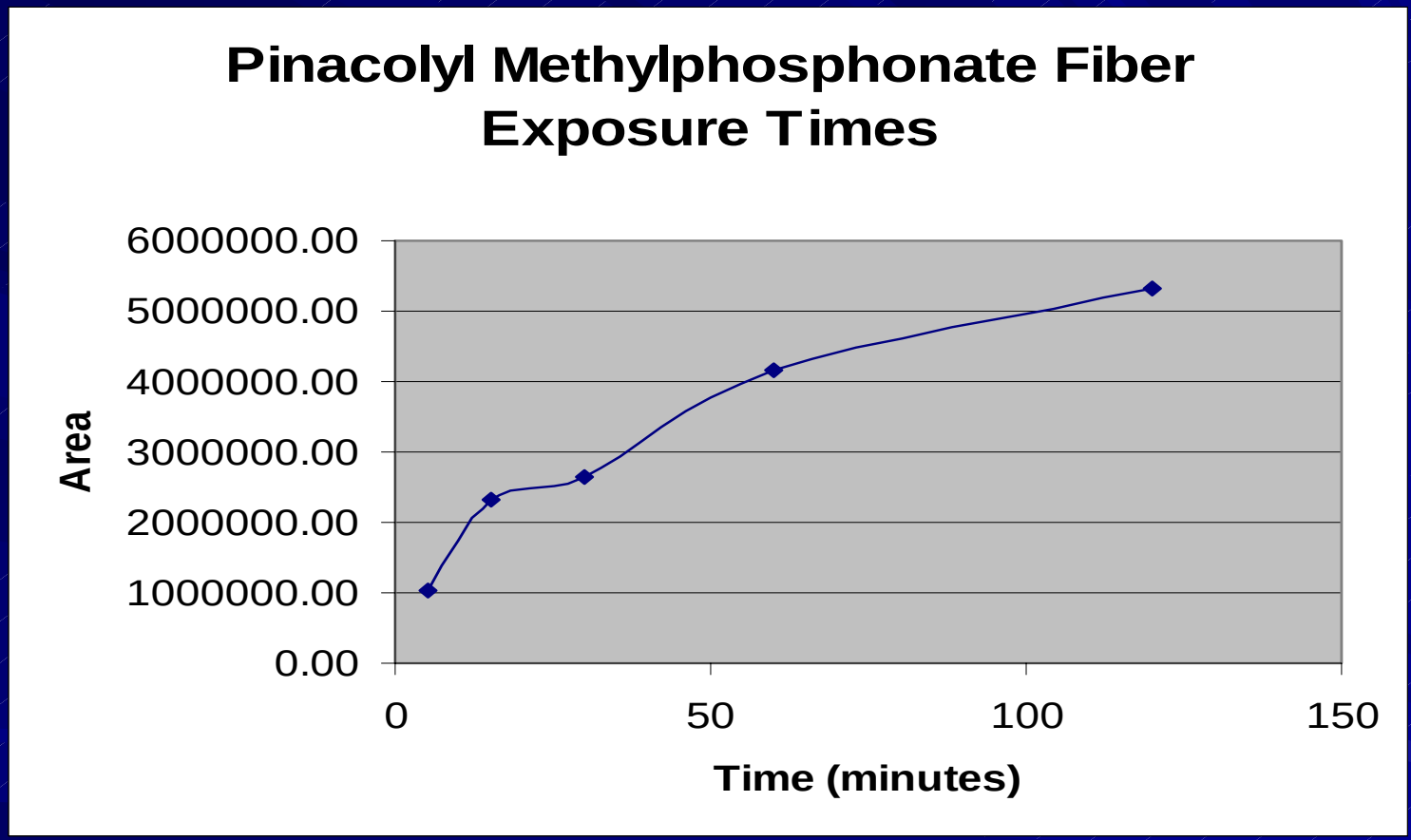
EMP Timed Exposure Study



IMP Timed Exposure Study



PMP Timed Exposure Study



Method Detection Limits

- Method Detection Limits (MDLs).
  - Used the EPA Method to determine the MDLs.
  - 40 CFR 136, Appendix B
  - 9 replicates were used,

Compound	*MDL*	*Standard Deviation*	*Average Recovery*
Ethyl Methylphosphonate	**29 µg/L**	**10 µg/L**	**104 %**
Isopropyl Methylphosphonate	**0.14 µg/L**	**0.048 µg/L**	**99 %**
Pinacolyl Methylphosphonate	**4.50 µg/L**	**1.5 µg/L**	**84 %**

Conclusion

- The calibration curves are linear with an r^2 value of at least 0.995.
- The analytes can be seen in the low µg/L range.
- The Analysis is very technique dependent.
  - Reproducibility of the placement of the fiber in the sample vortex is critical.
  - Timing of the fiber exposure has to be reproducible.